The University of Chicago

THE STRUCTURE OF α-QUARTZ

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
1935

BY
P'EI-HSIU WEI

JUNE, 1935

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The Structure of α-Quartz.

By P'ei-Hsiu Wei in Chicago.

Introduction.

The structure of α-quartz has been studied by various investigators[1, 2, 3, 4]). It belongs to the space group D_3^4 or D_3^6 according to whether it is left-handed or right-handed. The unit cell contains three silicon-dioxide molecules arranged spirally about the screw axis of symmetry. Its axial units are $a = b = 4.90_3$ Å and $c = 5.39_3$ Å. Its structure involves four unknown parameters designated analytically as u, x, y, and z by Wyckoff.

On account of various difficulties the exact values of the unknown parameters have never been determined. Gibbs attempted to narrow down the uncertainty in the parameter values in his paper of 1926[3]), but did not indicate its range. As pointed out by Ewald and Hermann[5]), his structure is not unique. It has thus been found impossible to apply his results in the study of various properties of α-quartz.

Considerable interest in the structure of α-quartz has been felt following the discovery by Bozorth and Haworth[6]) of its crystalline perfection. They measured the spectral width of *MoK*α lines reflected from an etched Curie cut quartz plate and found it to agree very closely with that predicted by Darwin's theory[7]) of reflection from perfect crystals. Their measurements were later confirmed by Parratt[8]). Quartz thus promises to replace calcite as reflector in the double crystal spectrometer in the study of X-ray spectra, and also to give a final test of the Darwin perfect crystal intensity formula, when its exact structure is known.

The present paper is an attempt at a more accurate determination of the said structure. Data were obtained by the usual method of oscillation photographs taken with a Bernal apparatus and indexed according to Bernal's method[9]). A set of absolute intensities including reflections

1) Bragg, W. H., Proc. Roy. Soc. London **89** (1914) 575.

2) McKeehan, L. W., Physic. Rev. **21** (1923) 206, 503—508.

3) Gibbs, R. E., Proc. Roy. Soc. London (A) **107** (1925) 561—570; Bragg, W. H., and Gibbs, R. E., Proc. Roy. Soc. London (A) **109** (1925) 405—427; Gibbs, R. E., Proc. Roy. Soc. London (A) **110** (1926) 443—455.

4) Wyckoff, R. W. G., Amer. J. Sci. **11** (1926) 101—112.

5) Ewald, P. P., and Hermann, C., Strukturbericht, Leipzig, 1931, 201.

6) Bozorth, R. M., and Haworth, F. E., Physic. Rev. **45** (1934) 821.

7) Darwin, C. G., Philos. Mag. (6) **27** (1914) 315.

8) Parratt, L. G., Rev. sci. Instrum. **5** (1934) 395.

9) Bernal, J. D., Proc. Roy. Soc. London (A) **113** (1926) 117.

of type $(h0l)$, $(00l)$, $(h00)$ and $(hk0)$ were also measured but were found useless in this analysis on account of the difficulty of reducing them to the structure factors. Every reflection listed in the following tables was recorded on several different exposures of the oscillation photographs. *MoK*-radiation was used. Laue photographs also gave valuable information of great help in the determination of the parameters.

Determination of Parameters.

It was found convenient to determine the silicon positions separately inasmuch as the effect of oxygen is relatively small for reflections with large values of $\sin\theta/\lambda$. By using reflections of this type it was possible to account satisfactorily for the observed intensities with a value of $167.5° \pm 1.5°$ for the silicon parameter.

Table I. Oscillation data at 0° plate position.

$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$	$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$
.120	100	vs	10.8	.372	301	vw	1.7
.152	101	vs	22.6		$30\bar{1}$	vs	31.4
	$10\bar{1}$	vs	37.8	.405	302	s−	12.2
.220	102	vs	7.0		$30\bar{2}$	s−	12.5
	$10\bar{2}$	vs	9.1	.454	303	w	8.9
.302	103	w	2.3		$30\bar{3}$	vw	1.0
	$10\bar{3}$	s	14.6	.416	220	s−	17.5
.208	110	s	17.6	.426	221	m−	11.0
.227	111	m	10.4		$22\bar{1}$	m−	10.4
	$11\bar{1}$	m	10.4	.455	222	vvw	1.7
.278	112	vs	21.6		$22\bar{2}$	nil	1.8
	$11\bar{2}$	—	21.9	.500	223	s−	15.6
.240	200	s	17.3		$22\bar{3}$	s−	15.6
.257	201	s−	11.5	.433	310	s−	20.9
	$20\bar{1}$	m	8.4	.443	311	w	5.7
.303	202	m	11.8		$31\bar{1}$	m	12.3
	$20\bar{2}$	s+	19.3	.471	312	m	11.6
.366	203	vs	31.2		$31\bar{2}$	s−	18.9
	$20\bar{3}$	s	14.8	.514	313	w−	6.9
.317	210	w	3.3		$31\bar{3}$	m−	8.8
.330	211	s	17.8	.480	400	m	9.9
	$21\bar{1}$	s	18.3	.489	401	s−	19.9
.367	212	s−	10.9		$40\bar{1}$	w	6.5
	$21\bar{2}$	s	21.7	.514	402	vw	2.3
.421	213	s	19.3		$40\bar{2}$	m−	12.0
	$21\bar{3}$	m	8.8	.554	403	m	17.8
.360	300	m−	5.8		$40\bar{3}$	m−	9.9

Table II. Oscillation data at 60° plate position.

$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$
.521	320	m−	11.3
.529	321	nil	1.5
	$32\bar{1}$	m	16.6
.553	322	m−	8.7
	$32\bar{2}$	tr	3.0
.550	410	vw	4.4
.557	411	m	14.5
	$41\bar{1}$	w−	10.0
.580	412	w	8.2
	$41\bar{2}$	w	8.1
.615	413	vw	4.4
	$41\bar{3}$	m−	16.9
.600	500	nil	.4
.610	501	nil	1.0
	$50\bar{1}$	w−	6.4
.628	502	m+	21.7
	$50\bar{2}$	nil	1.4
.661	503	nil	1.5
	$50\bar{3}$	nil	3.2
.634	420	m−	13.3
.641	421	vw−	6.6
	$42\bar{1}$	w−	8.2
.661	422	vw	5.2
	$42\bar{2}$	w	9.5
.670	510	w−	7.7
.675	511	m−	12.6
	$51\bar{1}$	w−	8.3
.694	512	vw−	3.3
	$51\bar{2}$	w−	8.1
.725	513	m−	12.0
	$51\bar{3}$	w+	10.7
.720	600	—	2.4
.724	601	m−	12.7
	$60\bar{1}$	tr	2.7
.743	602	w−	9.3
	$60\bar{2}$	vw	6.9
.771	603	vw−	2.4
	$60\bar{3}$	w+	11.7
.750	520	nil	.8
.755	521	nil	3.6
	$52\bar{1}$	m−	12.5
.773	522	w+	10.5
	$52\bar{2}$	w−	8.6
.800	523	vvw	5.7
	$52\bar{3}$	nil	1.2
.785	610	w	8.1
.789	611	vw−	4.4
	$61\bar{1}$	vw	7.7
.806	612	vvw	3.0
	$61\bar{2}$	w	12.0
.832	613	vvw	6.7
	$61\bar{3}$	vvw	7.0
.865	532	vw	6.6
	$53\bar{2}$	vvw	3.3
.889	533	w	15.1
	$53\bar{3}$	vw	5.5
.840	700	w−	9.8
.844	701	nil	1.7
	$70\bar{1}$	w	8.7
.860	702	vw	6.8
	$70\bar{2}$	nil	1.0
.884	703	nil	2.4
	$70\bar{3}$	nil	4.0
.859	620	vvw	.5
.865	621	vw	5.3
	$62\bar{1}$	vw	8.9
.880	622	nil	3.9
	$62\bar{2}$	vw+	9.6
.904	623	vw	6.0
	$62\bar{3}$	vvw	4.0
.905	710	w−	8.4
.909	711	vvw	5.3
	$71\bar{1}$	vvw	5.5
.924	712	nil	2.8
	$71\bar{2}$	nil	1.5
.947	713	vw	7.7
	$71\bar{3}$	vw−	5.7
.920	540	tr	4.6
.924	541	vvw	6.0
	$54\bar{1}$	vw	8.8
.939	542	vw	7.6
	$54\bar{2}$	nil	1.2
.950	630	vw−	6.0
.954	631	vvw	2.6
	$63\bar{1}$	nil	3.3

Table II (continuation).

$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$	$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$
.968	632	vw−	7.7	1.040	550	vw+	14.3
	$63\bar{2}$	vw−	7.9	1.044	551	nil	.8
.964	801	w−	9.1		$55\bar{1}$	nil	.6
	$80\bar{1}$	nil	1.4	1.057	552	—	2.4
.978	802	nil	2.2		$55\bar{2}$	—	2.0
	$80\bar{2}$	nil	1.4	1.050	640	tr	4.7
.980	720	nil	1.5	1.053	641	vvw	9.0
.983	721	vw−	5.3		$64\bar{1}$	tr	4.9
	$72\bar{1}$	vw	8.7				
.998	722	vw−	5.5				
	$72\bar{2}$	nil	4.5				

Table III. Laue data.

$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$	$\frac{\sin\theta}{\lambda}$	Index	Observed Intensity	Calculated Intensity $\lvert F \rvert$
.421	213	s	19.2	.521	320	m	11.3
	123	m−	8.8	.529	321	vvw	1.5
.490	214	s−	15.4		231	s	16.6
	124	w	4.2	.553	322	m	8.7
.560	215	vvw	3.6		232	vvw	3.0
	125	w+	14.2	.640	324	w+	7.7
.640	216	vvw	4.7		234	s−	18.6
	126	m	12.5	.700	325	m+	17.0
.372	301	w	1.7		235	w−	7.1
	031	vs	31.4	.550	410	vvw	4.4
.433	310	s	20.9	.557	411	m+	14.5
.443	311	w+	5.7		141	vw	10.0
	131	s−	12.3	.580	412	vw	8.2
.471	312	m	11.6		142	vw	8.1
	132	s−	18.8	.628	502	s	21.7
.514	313	w−	6.9		052	nil	1.4
	133	w+	8.8				
.489	401	vs	19.9				
	041	m−	6.5				

For reflections with small values of $\sin\theta/\lambda$, the effect of the oxygen atoms on the structure amplitude is large, and even for high order reflections the effect is far from negligible. It was therefore possible to locate the oxygen atoms with fair accuracy.

Approximate parameter values were found from considerations based upon interatomic distances. These values were then changed so

as to continually improve the agreement between observed and calculated intensities of reflection.

The best values were finally found to be:

$$x = 150° \pm 5° \quad y = 100° \pm 5° \quad z = 40° \pm 5°$$

Table II was obtained by turning the photographic plate to 60° from its usual position perpendicular to the incident beam, in order to bring large angle reflections inside the plate.

The atomic f-values used in computing the structure factors were those given by James and Brindley[1]). Bragg and West[2]) have given slightly different empirically determined f-values from other crystals. For quartz the deviations should not be important. (This has been verified by computation.)

Gibbs' result when converted to the usual analytical notation is as follows:

$$u = 165° \quad z = 40° \quad \left.\begin{matrix} x = 157° \\ y = 103° \end{matrix}\right\} \text{ or } \left.\begin{matrix} x = 207° \\ y = 122° \end{matrix}\right\}$$

Thus the x and y parameters were not uniquely determined by Gibbs. Ewald and Hermann have apparently made a miscalculation in giving the following pair of x and y values for Gibbs' result:

$$\left.\begin{matrix} x = 72° \\ y = 54° \end{matrix}\right\} \text{ or } \left.\begin{matrix} x = 112° \\ y = 94° \end{matrix}\right\}$$

Discussion of Structure.

The structure is based on the tetrahedral arrangement of four oxygen atoms around a silicon atom. The small distortion of the tetrahedron is within limit of error of observation.

Interatomic distances are: $Si-O = 1.61$ Å, 1.62 Å, 1.60 Å, 1.62 Å; $O-O = 2.62$ Å, 2.64 Å, 2.64 Å, 2.67 Å. The

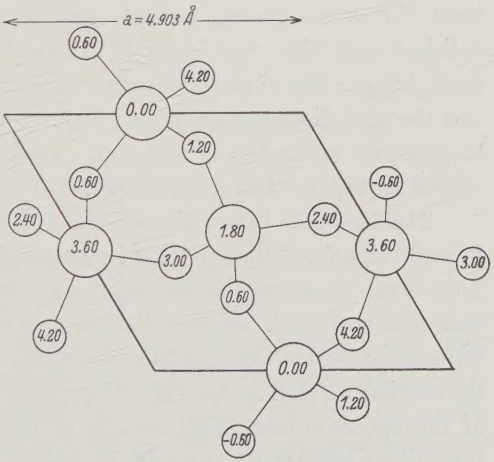

Fig. 1. Projection of structure on basal plane.
Small circles = O-atoms,
Large circles = Si-atoms,
Numbers = height above basal plane.

1) James, R. W., and Brindley, G. W., Philos. Mag. **12** (1931) 104.

2) Bragg, W. L., and West, J., Z. Kristallogr. **69** (1928) 118.

$Si-O$ distances observed agree well with results obtained from silicates.

The angle between the four bonds of silicon is practically a tetrahedral angle. The angle between the two bonds of oxygen is 144°. If the crystals were purely ionic, one would expect 180° between the bonds. On the other hand, the covalent type of binding would tend to make the bonds of oxygen at right angles to each other[1]). The fact that the observed angle is intermediate between the two extremes (180° and 90°) indicates that the binding is intermediate between the ionic and covalent type.

It may be noted that in the above structure the silicon positions are derived from those in α-quartz merely by a rotation of 6° 52′ about the screw axis of symmetry.

On the Extinction Coefficient of α-Quartz.

The writer has also made a series of absolute intensity measurements in the hope of obtaining some information regarding the extinction coefficient of α-quartz. This was intended to enable him to reduce a separate set of absolute intensity measurements (as indicated in the introduction above) for quantitative structure determination.

The crystal specimens consist of (a) a slab $5 \cdot 15 \cdot 30$ mm.^{3} cut with its large face parallel to a prism face and (b) six sections of varying thicknesses cut perpendicular to the threefold axis. All specimens were cut from the same quartz crystal, ground with No. 302 emery powder, polished and then etched in 48 per cent hydrofluoric acid solution for three hours. Each plate was examined under microscope after etching and the etch figures were found to have the same shape and orientation throughout each face examined. Optical examination also did not reveal any flaw in the specimens.

The absolute intensities of the 100 reflections were obtained both by reflection from the slab and by transmission through the thin sections. They were measured in the usual way with a Bragg spectrometer and rock salt standard. MoK-radiation was used throughout. The sections were mounted on the spectrometer table and adjusted until the plane of the section as well as the reflecting plane were both parallel to the axis of the spectrometer. Full details of this method of measurement have been described by Bragg and West[2]).

1) Slater, J. C., Physic. Rev. **37** (1931) 481; Pauling, L., J. Amer. chem. Soc. **53** (1931) 1367.

2) Loc. cit.

If the crystal can be treated as mosaic, then according to Darwin[1]) the integrated intensity is,

$$\varrho = Qte^{-\mu t}$$

where

$$Q = \left(\frac{Ne^2}{mc^2}\right)^2 \lambda^3 F^2 \frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$$

and μ is the effective absorption coefficient. The effective absorption coefficient is given by

$$\mu = \mu_0 + gQ$$

where μ_0 is the normal linear absorption coefficient and g is the extinction coefficient. Then we may write,

$$\log\ (\varrho/t) = \log\ Q - (\mu_0 + gQ)t$$

i. e. for a given reflection, $\log\ (\varrho/t)$ is a linear function of t, whose first derivative gives the extinction coefficient g. The normal linear absorption coefficient $\mu_0 = 10.0$ was determined separately. Fig. 2 shows $\log\ (\varrho/t)$ plotted against t. The markedness of its curvature clearly indicates the importance of primary extinction for α-quartz and affords a strong evidence against treating it as mosaic.

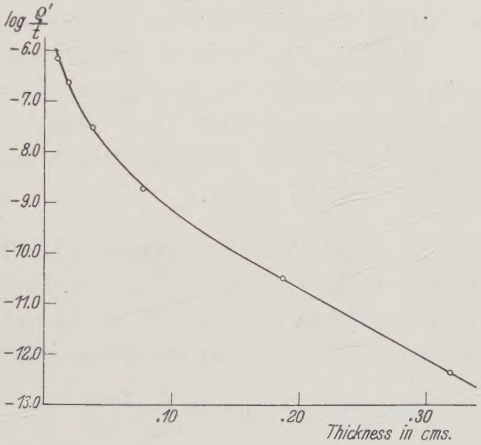

Fig. 2. Extinction Curve.

Darwin's perfect crystal formula was next tried where the integrated intensity is

$$\begin{aligned} \varrho &= 4/3\ (Ne^2/mc^2)\ \lambda^2 F\ \cot\theta \qquad \theta < 45° \\ &= \quad \text{»} \quad\ \tan\theta \qquad \theta > 45° \end{aligned}$$

Here the symbols have the same meaning as before. It was found that the observed intensities are proportional to the structure amplitudes (rather than the square) as required by Darwin's theory, but about five times greater than the computed values. While this shows that the quartz crystal used comes closer to the perfect than to the imperfect type, conversion of these observations to structure factors by means of

1) Philos. Mag., (6) **27** (1914) 675.

the perfect crystal formula is impossible. Nor is it possible (as we have seen) to reduce the observations by means of the imperfect crystal formula, since there is no way of correcting for the primary extinction. For the large number of crystals which lie between perfection and imperfection, and whose intensities of reflection are oftentimes so difficult to interpret, the development of a new intensity formula seems very desirable.

Summary.

α-quartz of the space group D_3^4 or D_3^6 has been found to have the following four parameter values:

$$u = 167.5° \pm 1.5° \quad x = 150° \pm 5° \quad y = 100° \pm 5° \quad z = 40° \pm 5°$$

Interatomic distances and angles between $Si-O$ bonds have been computed from this structure and found to be very reasonable.

An extinction curve of great curvature was obtained showing that primary extinction was important in the quartz crystal used. Absolute intensities of type $(hk0)$, $(h0l)$, $(h00)$, $(00l)$ were measured and found proportional to but about five times greater than those computed from perfect crystal formula.

In conclusion the author wishes to express his indebtedness to Professors A. H. Compton and W. H. Zachariasen for suggesting the problem and to Professor W. H. Zachariasen for his generous advice and constant interest in this investigation.

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